

# SCIENCE FOR GLASS PRODUCTION

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## SURFACE PHENOMENA IN GLASS TECHNOLOGY (A REVIEW)

**Yu. A. Guloyan<sup>1</sup>**Translated from *Steklo i Keramika*, No. 5, pp. 10 – 18, May, 2006.

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The perceptible role of surface phenomena in technological processes, including glass production, is discussed. Various glass technologies have their specifics, and, accordingly, surface phenomena have their specifics as well. So far this field of research has not been sufficiently investigated and requires more attention. Data on the role of surface phenomena in glass production processes and in service of glass products are offered. The possibility of using surface phenomena in traditional and new technological processes is analyzed.

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Surface phenomena at the phase boundary play a significant role in a multiphase system. Any interface surface significantly differs in its physicochemical properties from the interior of each phase. This difference is caused by the specifics of particle interactions at the phase boundary.

The main fundamental principles of the physical chemistry of interface surfaces are stated in the studies of T. Young (1805) and D. Gibbs (1872). Young described a boundary surface assuming that its mechanical properties are close to the properties of a hypothetical stretched membrane that has surface tension. Its position is selected so as to make this simple model equivalent to the complex domain existing between two contacting volume phase. Gibbs considered this problem in the thermodynamic context and introduced a geometric surface (the Gibbs dividing surface), which made it possible to provide an adequate mathematical description of this domain.

Substantial interest in surface phenomena stimulated extensive research in this field. Several fundamental studies described the general regularities of surface phenomena and results of scientific investigations [1 – 6].

Surface phenomena play a significant role in numerous technological processes, including the production of glass. The description of technological processes producing different types of glass, the characteristics of main surface phenomena, and data for calculating surface tension in glass melts are given in [7] (hereafter we mainly refer to reviews containing lists of original papers).

To a large extent the general regularities of surface phenomena are applicable to glasses as well; however, the spe-

cifics of the composition and structure and a high viscosity of melts create conditions for nonequilibrium surface tension in the course of the technological process. According to experimental data, the pattern of variation of some physicochemical properties of glass changes significantly within the so-called anomalous interval, i.e., within the transitory range between the melted state and the solid state. The same can be expected of surface phenomena as well, although direct evidence is missing due to significant experimental difficulties.

The most extensive experimental data are available for melted glasses and their interaction with solid bodies; data on solid glasses are much more scarce. Yet the technological significance of surface phenomena is high. Therefore, we will analyze the role and specifics of surface phenomena in glass production processes.

### SURFACE AND INTERPHASE PHENOMENA WITH PARTICIPATION OF MELTS

**Determination and estimate of surface characteristics.** The surface characteristics of liquids (melts) are easier to determine than those of solid bodies. A fundamental property of a liquid (melt) – gas interface, which is the most accessible for measurements, is its surface tension.<sup>2</sup>

Numerous methods for measuring surface tension are known. They have been theoretically substantiated and described in the above-mentioned studies.

Not all methods are suitable for measuring surface tension of highly viscous glass melts. Furthermore, substantial difficulties are involved in high-temperature measurements.

<sup>1</sup> Scientific Research Institute of Glass, Gus-Khrustal'nyi, Vladimir Region, Russia.

<sup>2</sup> The “interfacial tension” is a more precise term; however, we will use here the generally accepted terminology: “surface tension” for the liquid – gas interface and “interfacial” tension for liquid (melt) interface.

Most measurement data of the surface tension of melts are obtained using the immobile drop method, the drop weight method, the maximum pressure in a bubble, or the immersed cylinder method. The principles of high-temperature measurements of surface tension of metal and slag melts, as well as the schemes of experiment plants for measuring surface tension in glass melts, are described in [8].

The interfacial tension at the boundary of two liquids (melts) can be determined using the methods related to drop formation at the interface: the maximum pressure in a drop, the drop weight, and the immobile drops. The methods of photography and roentgenography of slag drops on a metal surface and drops of metals under a slag layer have been developed specially for high-temperature melts (metal – slag) [8]. The method of x-ray photography of a metal drop under a glass layer was applied to measuring the interfacial tension at the glass melt – metal melt phase boundary [9].

Numerous researchers have focused on measuring the surface tension of glass melts. Many of them, especially the earlier ones, are systematized in V. Eitel's book [10] and later works are listed in reference book [11]. Systematic studies of surface tension as a function of the composition (including small additives) and temperature were started by A. A. Appen and A. Badger with colleagues (1936, 1937) and carried on by A. Ditzel (1942) and K. Rubinstein (1964). These studies were used to develop a method for calculation and classification of glass components based on their effect on surface tension [12, 13].

Additional information on the phase boundary can be obtained by studying electrocapillary phenomena. There is an electric double layer on the boundary of molten metals with slag, glass, or salt melts, which produces a potential jump when an external electric field is applied and, consequently, changes the interfacial tension. Numerous studies of electrocapillary phenomena have been done for melts used in ferrous and nonferrous metallurgy. Some results are described in [14]. It would be interesting for glass technology to study electrocapillary phenomena at the boundary between glass and some low-melting metals, but such research has not been systematically carried out.

Apart from surface and interfacial tension, the interaction at the interface can be estimated using the concept of adhesion (interaction at the boundary of two phases) and cohesion (interaction inside one phase). In a contact of glass with tin:

$$\left. \begin{aligned} A_a &= \sigma_t + \sigma_g - \sigma_{g-t}; \\ A_g &= 2\sigma_g; \\ A_t &= 2\sigma_t, \end{aligned} \right\} \quad (1)$$

where  $A_a$  is the adhesion work;  $A_g$  and  $A_t$  is the cohesion work for glass and tin;  $\sigma_g$  and  $\sigma_t$  is the surface tension of glass and tin at the boundary with the gaseous phase; and  $\sigma_{g-t}$  is the interfacial tension at the glass – tin boundary.

These characteristics were used in developing the float process to estimate the interaction of glass with tin and for

electrochemical treatment of thermally polished glass ribbon using melts of metals and salts [15 – 18].

Surface tension is directly related to adsorption on the surface of a liquid (melt). The quantitative relation between surface tension and adsorption is expressed by the Gibbs equation

$$\Gamma = -\frac{a}{RT} \frac{d\sigma}{da},$$

where  $\Gamma$  is the absorption value;  $a$  is the activity (concentration can be used for diluted solutions);  $R$  is the universal gas constant; and  $T$  is the absolute temperature;  $\sigma$  is the surface tension.

The value  $-d\sigma/da$  or  $-d\sigma/dc$  determines the rate of decrease in surface tension depending on the activity (concentration) of the component in the solution (melt). It is called surface activity.

According to A. A. Appen [13], all oxides of glass-forming melts are classified into three groups based on their effect on the surface tension. Surface tension in melts formed from the components of the first group has a simple approximately additive dependence. For glasses containing components of the second and third groups a simple calculation of surface tension is impossible. Due to the adsorption of these components on the surface, the composition of the surface layer differs from the volumetric melt composition, whereas surface tension decreases to some extent. The CLTE in this case may have the opposite, i.e., the positive sign, which is also determined by adsorption phenomena.

Classifying components into groups has a certain theoretical substantiation [13]. The first group includes glass-forming oxides ( $\text{Si}_2\text{O}$ ,  $\text{GeO}_2$ , etc.) and metal oxides having a relatively high energy level of the Me – O coordination bond in polyhedrons  $[\text{MeO}_k]$ . The third group includes oxides that form discrete disjoint complex anions  $(\text{MeO}_n)^{x-}$  inside which the bonds are especially strong. Such anions, namely,  $(\text{CrO}_4)^{2-}$ ,  $(\text{MoO}_4)^{2-}$ ,  $(\text{WO}_4)^{2-}$ ,  $(\text{SO}_4)^{2-}$ , and  $(\text{VO}_4)^{2-}$ , are strong structural elements, but their interaction with each other is insignificant. Therefore, adsorption layers formed by them perceptibly decrease the surface tension of the melt. The intermediate second group includes oxides of a dual nature. These are primarily components with the lowest bond energy ( $\text{K}_2\text{O}$ ,  $\text{RbO}$ ,  $\text{Ca}_2\text{O}$ ,  $\text{Ti}_2\text{O}$ ,  $\text{PbO}$ ). Secondly, these are components which in a silicate melt form complex discrete anions  $(\text{SbO}_4)^{3-}$ ,  $(\text{BiO}_4)^{3-}$ , and  $(\text{BO}_4)^{5-}$  that are less strong than the third group anions mentioned above (some researchers also assume the formation of molecules  $\text{Sn}_4\text{O}_6$ ,  $\text{B}_4\text{O}_6$ ,  $\text{Bi}_4\text{O}_6$ , etc.).

Adsorption phenomena in glass melts play a significant role in glass melting and glass forming processes. The structural heterogeneity of glass melts leads to a nonuniform distribution of additives and impurities among their structural components. This phenomenon known as internal adsorption [19] is manifested, in particular, in a perceptible effect of

small impurities, including dissolved gases on the structure-sensitive properties of glass melts.

**Surface phenomena in technological processes.** Below we consider surface phenomena in melts formed in glass melting or in melting solid glasses.

*Glass melting.* In the beginning of glass melting, melts obtained in silicate formation have a perceptible degree of heterogeneity regarding their chemical compositions and the presence of a large number of unmelted particles and bubbles. Such melts have a clearly cellular structure, whereas surface forces acting on their interfaces continuously modify these interfaces and facilitate the homogenization of the glass melt simultaneously with the effect of rising bubbles. The glass melt surface as well has perceptible inhomogeneities with different surface tension parameters. At the same time, an intense continuous surface exchange takes place involving the volume layers adjacent to the surface in this process as well.

There is an effect known as the “Marangoni effect” where liquid is displaced inside a volume under the effect of surface (interfacial) tension. This effect is characterized by the dimensionless Marangoni criterion:

$$\text{Ma} = \frac{\Delta\sigma L}{\eta D}, \quad (2)$$

where  $\Delta\sigma$  is the surface (interfacial) tension gradient;  $L$  is the characteristic length;  $\eta$  is viscosity; and  $D$  is diffusion.

It follows from (2) that the motion of a liquid (melt) under the effect of surface tension is directly related to the main kinetic parameters at the phase boundary: the viscosity and the mass transfer rate. The “Marangoni effect” is manifested in glass melting and in the contact of glass melt with refractory materials.

The glass melt motion under the effect of surface forces was investigated using model fluids by H. Jebsen-Marwedel (1948 – 1956) and R. Bruckner (1961 – 1968, 1980). The results of this studies are summarized in [20]. A vortical motion of low-viscosity model liquids under the effect of surface tension has been registered. Clearly, such vorticity is impossible in high-viscosity glass melts, but significant migrations occur on the phase boundary. Furthermore, one should take into account the nonequilibrium surface and interfacial tension values in high-viscosity melts [9].

Laboratory experiments, as well as industrial practice, have registered mass transfer processes at phase boundaries under the effect of variations in density, redox conditions, or chemical composition of the surface layer caused by the volatilization of particular components ( $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{Na}_2\text{O}$ , etc.). Some typical glass melt defects (striae) arise in melting lead-silicate glass in tank furnaces for making household and fancy glass despite the mixing of the glass melt in the working zone of the furnace. A variation in the composition and density of the surface layer caused by the volatilization of components, primarily of lead oxide, increases the surface

tension and causes the formation of striae. Only intense mixing of glass during its melting and cooling provides stria-free glass suitable for optical glass technology.

There are interesting data from experiments and industrial observations on interface mass transfer occurring as a consequence of varying redox conditions in glass melting [20]. The reducing conditions, particularly in the gaseous atmosphere of the furnace, contribute to increasing surface tension of the glass melt (up to 20%). In this case the surface layer has to be displaced into the melt volume and the volume layers rise to the surface. This rather intense transfer occurs as a consequence of surface “discontinuities.” An uncontrolled variation of redox conditions may produce glass melt defects in the form of cords, bubbles, or local tinting [20]. The role of surface tension in clarification, homogenization, and formation of secondary bubbles is also described in [20].

The formation of secondary bubbles in a glass melt is related to the degree of its saturation by chemically dissolved gases, whose solubility decreases with increasing temperature. Gas bubbles arising in a liquid (melt) are capable of subsequent growth only if their radius has reached a critical value. The critical radius of the bubble is extremely sensitive to surface tension and the degree of supersaturation of the liquid (melt). Therefore, the formation of secondary bubbles  $\text{SO}_2$  and  $\text{O}_2$  (under repeated heating of the glass melt) is usually observed in glass melts melted with sodium sulfate (significant supersaturation in  $\text{SO}_3$  dissolution and a decreased surface tension in the formation of bubbles:  $\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2$ ). Under these conditions the role of the chemical heterogeneity of the glass melt and its surface layer significantly grows, since the formation of bubbles on interfaces is easier.

*Glass forming.* The role of surface phenomena in glass forming under isothermic conditions is significant and grows as the size of articles decreases. The methods for forming glass microballs (GMB) and hollow glass microspheres (HGM) of diameters 0.05 – 2.00 mm are fully based on the effect of surface forces.

In producing GMB from a melt, a thin glass jet breaks into discrete drops under a centrifugal force or a gas jet and then forming is completed in the thermal chamber. The majority of GMB, especially small ones, are produced by fusing premilled glass in a gas burner flame. When HMS are formed from a glass powder, the motive force transforming solid glass particles into hollow microspheres is the thermal dissociation of  $\text{SO}_3$  dissolved in glass. This process occurs at a temperature above 1000°C in a reducing atmosphere.

Thus, surface forces fully form a microsphere, both from inside and from outside. The surface force in this case overcomes gravity and viscous resistance force. The rate of acquiring a spherical shape depends on temperature and the respective glass viscosity [21]. The process of producing GMB and HGM is discussed in more detail in [22, 23]. A similar surface force effect occurs in free formation of fine toroidal bead articles from tubular preforms [21].

The first stage of the float process, i.e., glass melt spreading over the surface of molten tin, proceeds under isothermal conditions. Spreading occurs by gravity; however, the surface forces restrict spreading and form edge zones in a lens of equilibrium thickness. An analysis of the physico-chemical factors in isothermal forming is found in [9, 21].

It should be noted that the interfacial tension on the glass-tin boundary as one of the factors of spreading and producing a high-quality glass surface has not been sufficiently studied. Data on experimental determination of interfacial tension are scarce. Some data from foreign researchers are cited in [15–17] without specifying the determination method. The results of domestic researchers determining interfacial tension on a glass–tin boundary using the x-ray analysis of a tin drop under a glass layer are described in [9]. The authors note the kinetic factor of establishing equilibrium interfacial tension due to the high viscosity of glass melt and slow establishment of adsorption equilibrium at the interface boundary. The same study gives data on glass–lead interfacial tension in the context of studying thermal treatment of lead crystal products.

Phenomena on the interface of glass and low-melting metals are highly significant for electrochemical modification of a moving ribbon of thermally polished glass [18]. Surface tinting of the glass ribbon takes place in its contact with alloys of lead, copper, and other low-melting metals under the effect of an electric field. In this case the interfacial tension changes and favorable conditions arise for accelerated diffusion of metals into the surface layer of the glass and its tinting.

In forming medium and large products under nonisothermal conditions, the shape of an article is formed by external factors (extrusion, rolling, blowing, compression, centrifugal effect) using restrictive devices (molds, rollers, etc.). The effect of the surface force in this case is reduced to smoothing small surface roughnesses and rounding the edge zones.

In forming glass fiber, the most important working parameter is the capacity for fiber formation. This parameter depends on the ratio of viscosity to surface tension [24]. However, the critical role here is played by viscosity, since its dependence on the composition and especially on temperature is significantly higher than that of surface tension. At the same time, surface tension contributes to forming a low-defect surface, which together with fast cooling and “freezing” a high-temperature structure ensures high strength in the continuous glass fiber. The surface phenomena are especially significant in extruding fiber light guides (from two types of glasses) using the die and the fillet methods. Staple fiber as well is formed by external forces (centrifugal force, blow energy) together with the surface force effect. In this case the glass melt has to have low values of viscosity and surface tension [24].

The surface force effect forms the basis for the production of foam glass [25], which is a coarsely disperse system (solid foam) whose gaseous phase is distributed in the solid

dispersion phase with a smaller volume (glass). Foam glass as a rule is produced from glass powder and foaming agents. The emission of gases starts at 750–950°C and they form cavities in a highly viscous glass melt. The pressure inside these cavities reaches substantial values according to the Laplace equation:

$$P = \frac{2\sigma}{r}, \quad (3)$$

where  $\sigma$  is the surface tension of glass and  $r$  is the gas cavity radius.

The shape of the cells containing the gaseous phase may be spherical, but more often it is polyhedral due to the pressure of gas in the adjacent cells. The lower the surface tension of glass, the better the foam formation, and the stability of foam is ensured by the high viscosity of glass. Furthermore, surface tension decreases due to adding sodium sulfate and other surfactants.

## SURFACE AND INTERFACE PHENOMENA WITH PARTICIPATION OF SOLIDS

**Methods for determining surface parameters.** One of the earliest quantitative results describing the properties of solid body surface is the equation derived by T. Young for the angle of a liquid wetting a solid body:

$$\begin{aligned} \sigma_{l-g} \cos \theta &= \sigma_{s-g} - \sigma_{s-l}; \\ \cos \theta &= \frac{\sigma_{s-g} - \sigma_{s-l}}{\sigma_{l-g}}, \end{aligned} \quad (4)$$

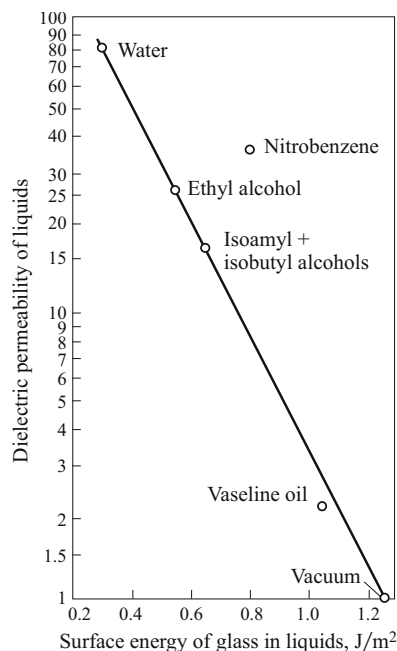
where  $\sigma_{l-g}$  is the surface tension at the liquid–gas interface;  $\sigma_{s-g}$  and  $\sigma_{s-l}$  are the surface and interfacial tension at the solid–gas and solid–liquid interfaces;  $\theta$  is the contact wetting angle.

The equation is derived based on projecting all forces on the solid body surface and equating the sum of these projections to zero. Other methods were developed later for studying the surface parameters of solid bodies based on estimating the work done on forming a new surface (by means of scratching, grinding, exfoliation, crack formation, milling and subsequent dissolution, etc.), as well as methods for calculating the surface energy of solids which, however, do not yield unambiguous results.

Experimental and calculation methods are reviewed in [2]. The same book describes in detail the results of research by V. P. Berdennikov (1934) on determining the surface energy of solid glass by the method of a crack formation in various media and in vacuum. Figure 1 shows the results of measuring surface energy in liquids with different dielectric permittivity and in vacuum. The obtained values vary from 0.3 J/m<sup>2</sup> (in water) to 1.26 J/m<sup>2</sup> (in vacuum).

Considering the process of glass destruction as the work done on the formation of a new surface, it should be noted that a freshly formed surface of glass is highly hydrophilic.





**Fig. 1.** Correlation between surface energy of glass in liquid and in vacuum and the logarithm of dielectric permeability of the liquid (according to V. P. Berdennikov).

Surface energy in forming a new surface significantly decreases in the presence of water or water vapor. The decreased work on glass destruction in grinding is due to the adsorption of water or its vapor in microcracks of the pre-destruction zone and these cracks becoming filled with gel-like reaction products which prevents their closure.

The dual definition of surface tension as the effect of an elastic deforming force and the work on forming a new surface is acceptable for liquids, for which these notions are identical. In the case of solid bodies these notions are independent of each other and suggest various approaches to surface phenomena, which are reviewed by A. Ya. Gokhshtein [3]. The author demonstrates that surface tension causes a deformation of solid bodies, although very small, of the order of a few atomic distances. A highly sensitive method has been developed making it possible to register the variation of the interfacial tension of solid electrodes in electrolyte solutions as a derivative of the interfacial tension of a conducting solid body based on the electric variable (the estance method). This method can be used for a deeper analysis of surface (interface) phenomena in solid glasses taking into account the studies of M. M. Shul'ts on glass electrodes.

At the same time, the author of [6] notes the impossibility of an experimental determination of surface tension in solid bodies and recommends using calculation methods, which are also described in [6].

In estimating the state of a solid surface, it is necessary to take into account the imperfection and inhomogeneity of the surface, surface mobility of particles, existence of surface groups, and adsorption of gases and vapors.

Considering the surface of solid silicate glasses, it should be noted that the surface glass layer 1 – 10 nm thick is totally different in its structure and composition from the volume glass layers. The assumption of a thin protection film present on the glass surface was first put forward by F. Milius (1907) and later corroborated by the detailed studies of I. V. Grebenshchikov with colleagues (1929 – 1937). The results of studies in this area are systematized in [26].

In forming glass products, a surface film is formed on glass due to the fast interaction of the surface with the ambient medium, mainly with atmospheric moisture. As a consequence of hydrolysis, a thin layer emerges on the glass surface, which consists of a silica skeleton filled with silicic acid gel and other products of chemical reactions. This layer protects glass from further destruction. The chemical composition of the surface layer depends on glass composition and, consequently determines its chemical resistance. One should take into account the negative consequences of the destruction of the surface layer in contact with food products, for instance, in violating manufacture and service conditions for some types of glass containers.

**Surface phenomena in technological processes.** In mixing batch materials and especially in batch moistening, wetting and capillary force prevent the stratification of the batch. Surface phenomena play an important part in consolidation of glass batches and hydrothermal treatment of amorphous rocks to produce liquid glass and homogenous batch mixtures for glass melting [27, 28].

**Glass melting and glass-melting furnaces.** In the initial period of glass melting an alkali melt reacts with solid  $\text{SiO}_2$ . Substantial chemical affinity and good wetting of quartz sand grains by the alkali solution lead to chemisorption and a fast chemical reaction via the formation of surface complexes and radicals with intense gas emission. The formation of bubbles depends on surface phenomena. The reaction kinetics and the ratio between the energy parameters of the surface and volume components of the chemical reaction are analyzed in [29].

One of the most significant processes in a glass-melting furnace is the interaction of silicate melts with refractory materials, whose intensity determines the service life of the glass-melting furnace and the quality of glass produced. A significant factor in the destruction of refractories is the effect of surface and interface phenomena at the phase boundary.

H. Jebesen-Marwedel (1967) believes the surface force on the boundary of three phases (refractory – melt – gaseous atmosphere) to be one of the main factors. According to R. Bruckner (1967, 1980), the maximum corrosion of refractory materials at the glass melt level is caused by intense motion of glass melt at the phase boundaries (convection in the boundary layer), where the surface and interfacial tension in the contact layer grows due to the growing content of  $\text{Al}_2\text{O}_3$  in this layer. The Marangoni effect is hereby manifested. The intense convection of the glass melt in the boundary layer, in turn, decreases the contact layer thickness, accelerates the

mass transfer rate, and increases corrosion intensity. The mechanism of the corrosion of refractories at the glass melt level was also investigated by I. Lefler in 1965 – 1967. Figure 2 shows the substantial role of wetting and drop formation processes that are nearly entirely determined by surface forces and chemical reactions.

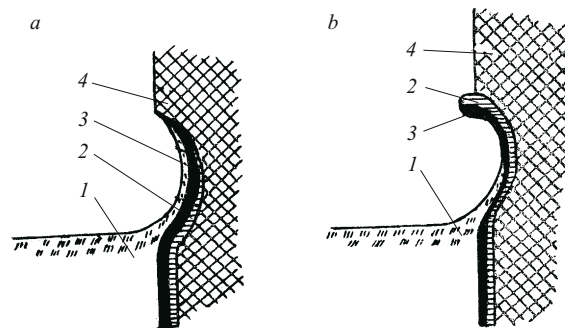
Surface phenomena also play a critical role in the vertical cellular corrosion occurring under the effect of gas bubbles. The variations of surface and interfacial tension at the phase boundary (and the Marangoni effect) leads to the rotary and reciprocating motion of bubbles with the constant renewal of the interface. This effect of the surface force accelerates the chemical interactions and mass transfer and leads to a high rate of vertical cellular corrosion. The results of studying the interaction between refractories and glass melts in melting are systematized in reviews [20, 30].

It is evident that corrosion of refractories in glass-melting furnaces, especially at the level of the glass melt surface, can be decreased by decreasing the differences in the interface tension in the contact layers and increasing viscosity at the phase boundaries. The corrosion of refractories can be slowed as well by decreasing the reaction capacity of the glass melt in the contact zone through decreasing the content of active components ( $\text{Na}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ , etc.) in the glass.

It should be noted, however, that the quality of refractories and their cooling at the glass melt level to raise the melt viscosity and delay the mass transfer process in the contact layers play a critical role in practical glass melting. To a certain extent the reaction capacity of a glass melt can be decreased by lowering the content of active components in glass. At the same time, the factor of decreasing the interfacial tension gradient in the contact layers is used with chromium oxide refractories whose high resistance is combined with the surface activity of chromium oxide.

**Forming glass products.** The role of surface phenomena in forming glass products has been considered above. Here we should note that surface defects, in particular, notches under mechanized blow molding and compression molding, emerge in the case of violation of the forming regime or unbalanced operation of the machinery. The stresses arising in such cases exceed the surface tension, local surface discontinuities are observed, and the crack propagates to a certain depth, which may cause the destruction of the product. In glass blowing, glass melt mainly contacts a thin layer of the products of decomposition of organic technological lubricants or a water steam-gas layer, when special mold coatings are used. The products of decomposition of organic lubricants have actually no effect on the surface layer of the glass article due to the large size of their molecules, the short time of contact, and the high rate of glass solidification. The quality of the surface determined by the surface force effect depends on the purity class mold surface finishing.

**Thermal treatment.** Surface phenomena play a critical role in processes related to the formation of a new phase in glass solidified after its molding. This primarily concerns



**Fig. 2.** Scheme of corrosion of refractory beams at the level of the glass melt surface (according to I. Lefler): *a*) start of the process; *b*) formation and start of the drop breaking off; 1) initial glass composition; 2) contact glass; 3) glass depleted of alkali oxides; 4) refractory.

catalyzed crystallization and formation of glass ceramic (devitrified) materials [31, 32].

The main requirements imposed on crystallization catalysts are as follows:<sup>3</sup>

- ensuring good wetting of the emerging seed by the matrix melt and decreasing the work on the formation of the seed;
- ensuring the required coordination of the crystal lattice parameters of the seed and the main crystallizing phase (the deviation should not be more than 15% in compliance with the crystallographic similarity principle).

The work of forming a critical seed (crystallization center) depends on the expression

$$A_{\text{cr}} = \frac{RB\sigma^3}{(\Delta T)^2},$$

where  $R$  is the gas constant;  $B$  is a constant depending on the physical properties of the material;  $\sigma$  is the surface (interfacial) tension; and  $\Delta T$  is supercooling.

It follows from the above equation that the deciding factor in the formation of a critical seed is played by the interfacial tension at the crystal – glass boundary. Therefore, interfacial tension can be controlled using crystallization catalysts for the purpose of raising the process efficiency and obtaining the required properties in glass ceramics.

A similar role is played by surface phenomena in opacifying and colloid tinting of glass, in reducing processes in lead-containing glasses, and in various processes occurring in light-sensitive, photochromic, and electrochromic glasses and glass ceramics [31, 32].

Surface forces play a crucial role in thermal treatment related to partial fusion of glass in articles, for instance, in fire cutting of caps, fusing edges, and thermal polishing of

<sup>3</sup> A catalyst in chemistry is understood as a substance accelerating a reaction but remaining unchanged. A crystallization catalyst simultaneously behaves as an accelerating agent and as a participant of the crystallization process.

molded articles and ground blown articles. The thin fusing glass layer under the effect of surface forces migrates along a solid substrate of the same glass and forms spherical surfaces under virtually perfect wetting of the substrate by the emjging melt.

There are numerous microcracks on the surface of industrial glass articles that decrease the strength and service reliability of articles. The dissolution of this defective layer and modification of the surface substantially increases the strength and service reliability of glass articles. It is possible to obtain a substantial improvement of the surface parameters of products and, consequently, their service reliability by treating their surface with salt solutions (ion exchange) and gaseous reactants. In doing so one can significantly improve the strength, thermal and chemical resistance, and other parameters of glass articles. Extensive information on modifying surfaces using salt solutions and gaseous media is systematized in [33, 34].

*Producing coatings on products.* Methods for producing coatings on different articles are numerous. The choice of a particular method depends on the shape and size of articles, the heating type and admissible heating limit of the coating, etc. Coatings used in glass production can be divided into two groups:

- vitreous coatings on products made of different materials (metal, ceramics, glass, etc.);
- nonvitreous coatings on glass articles.

It should be noted that coatings are usually applied to articles in contact with a melt and its subsequent solidification or from a vapor–gas phase [35].

The main characteristics for depositing coatings are adhesion and cohesion. The generalized expressions characterizing adhesion and cohesion are given in Eqs. (1). The interaction between an adhesive and a substrate consists of several stages [35].

*Wetting.* Wetting conditions in the general form are characterized by Young's equation (4) which indicates that the contact wetting angle can serve as a measure of the wetting of a solid body by a liquid (melt). The values of parameters characterizing wetting can vary in time if the liquid (melt) reacts with the solid body or has high viscosity. The emergence of physical forces of attraction or a chemical bond between the adhesive and the substrate are the primary stages of interaction. In this period adsorption reactions take place and an active surface complex is formed.

The subsequent stages (sticking of liquid (melt) to the solid body and contact joining of solid bodies) are also closely related to surface phenomena. These are initial adhesion stages. A strong adhesion of the surface with the solid substrate is a very important condition of an adequate service of the coated article. Adhesion is a consequence of secondary process starting from the surface and evolving into the depth of the material. They include chemical and electrochemical reactions, dissolution, diffusion, etc. These processes modify the surface relief, form new products, modify the concentration of the initial components at the interface, etc. At that

time intermediate layers of a certain thickness are formed. The emergence of a new transition layer (one, two, or more) between the coating and the substrate is a typical characteristic of adhesion. In this process, interface boundaries may arise: coating – transition layer; transition layer – transition layer, or transition layer – substrate. These boundary interfaces may be blurred or relatively clearly expressed.

The strength of adhesion is measured by the force required to tear a coating off its substrate. Such break-off may occur along an interface (adhesion break) or across the transition layer and even across the material of the coating or the substrate (cohesion break). This break may be a combined one as well.

The specified stages of physicochemical interaction are implemented in the processes of depositing vitreous coatings on metal, ceramic, glass, and other articles. Various methods of deposition can be used: depositing solid-liquid composites on a prepared surface and subsequence firing (deposition of enamels, glazes, and paints); deposition of soluble coatings on cold or heated articles (production of mirrors, thermos flasks, sol-gel process for special coatings, etc.); production of glass coatings on the inner surface of metal pipes, etc. The original method for producing microcables in an insulating glass shell is based on simultaneously extruding a glass tube into a capillary and filling its opening with molted metal. The metal is entrained by the surface of the extruded glass capillary as a consequence of adhesion, which is intensified when surfactants are added to metal.

Metal, oxide, and other types of coatings can be deposited on glass from a vapor-gas phase in vacuum by electrothermal and gas-discharge spray deposition. The processes of evaporation, condensation, and formation of coating, as well as the strength of its adhesion to glass, are determined by surface phenomena.

*Contemporary nanotechnologies* are virtually totally based on surface phenomena. For instance, the sol-gel technology of nanodisperse silica makes it possible to obtain extra pure or alloyed quartz glass, fiber light guides, optical coatings, and other materials and products with unique properties and a controllable structure [36]. The presence of a highly extended surface and reaction-capable silanol groups on disperse silica particles makes it possible to modify sols by adsorption methods and thus to obtain the required properties in coatings and products. In producing fiber light guides based on quartz glass, surface forces form modified light-guiding and light-insulating layers on the inner surface of the tube under the thermal decomposition of silicon tetrachloride with alloying additives. A consecutive deposition of these layers in extruding the tube ensures the production of a fiber light guide as the opening “collapses” under the effect of surface forces.

A brief review cannot encompass all the varieties of surface phenomena: they are present in each technological process but insufficiently investigated.

The attention of researchers in the studies cited is focused on establishing a relationship between the measured



parameters (surface and interfacial tension, contact wetting angle, adsorption, etc.) and the surface layer structure, as well as analyzing the factors of the process. Such research has led to a significant advance in studying surface phenomena and using them in technological processes.

Considering the results of studying the structure of the surface (interface) layer, an interface can be represented not as just a geometric surface but as an intermediate phase of a certain thickness. Glass and its surface layer can be a typical example.

Glass, glass ceramics, and composite materials based on them are widely used in construction, different sectors of industry, medicine, and household. Therefore, one of the most important directions in material science is studying the service of materials and products in particular conditions and the specifics of surface phenomena at phase boundaries. For instance, surface (interface) processes in contact with a living organism are significant for bioactive vitreous and glass ceramic materials.

To increase the efficiency of using composite materials, it is necessary to systematically study the interface of the glass or glass ceramic matrix and the reinforcing filler. Contemporary nanotechnologies are based on surface (interface) processes, and their further increase in efficiency is related to studying the surface and interface phenomena at the phase boundaries.

Unfortunately, little attention is paid to direct studies of surface phenomena in glass production processes and in service of glass products, especially in domestic applied science. Undoubtedly, a deeper study of surface (interface) phenomena correlated with production technology and application of diverse glass articles could be a key to solving not only theoretical issues but also topical applied problems, for instance, a substantial increase in strength and service reliability of glass and glass products.

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